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# UK Patent Application

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(56) Documents cited  
GB 2123965 A GB 2085592 A EP 0084874 A  
WO 87/06009 A US 4339719 A

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## (54) Method and apparatus for measuring the type and concentration of ion species in liquids

(57) Ion species in a liquid are identified by placing two spaced apart electrodes in the liquid, applying a voltage between the electrodes which is greater than  $qNd^2/2E$  where q=the charge on the electron, N is the highest ion concentration expected, d is the distance between electrodes and E is permittivity of the liquid. The interval(s) between the cessation of charging current due to capacitance between the electrodes and one or more subsequent falls in the current which then flows between the electrodes are measured to identify the ions.

The magnitude of each fall is characteristic of the concentration of an ionic impurity in the water and the time at which the fall occurs indicates the type of ion.

In an embodiment of the present invention, a cell based on a silicon substrate 25 has electrodes 30 to 33 carried on ridges in the substrate separated by grooves 26, 27 and 28. In operation, water to be analysed for ionic impurities fills the grooves.

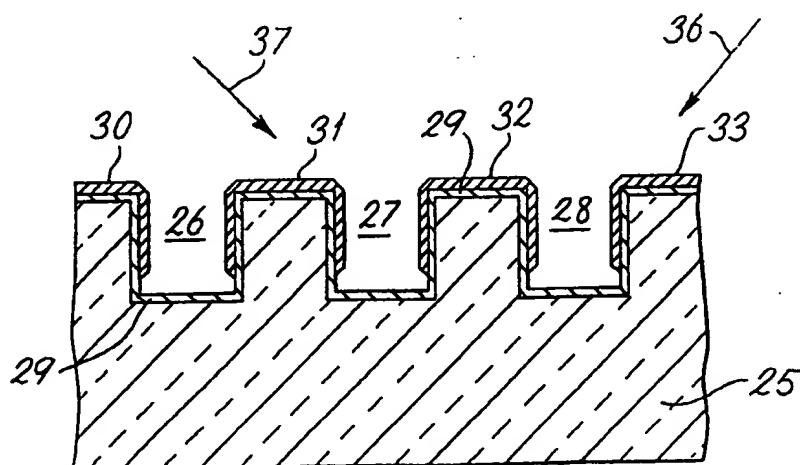


Fig. 2a

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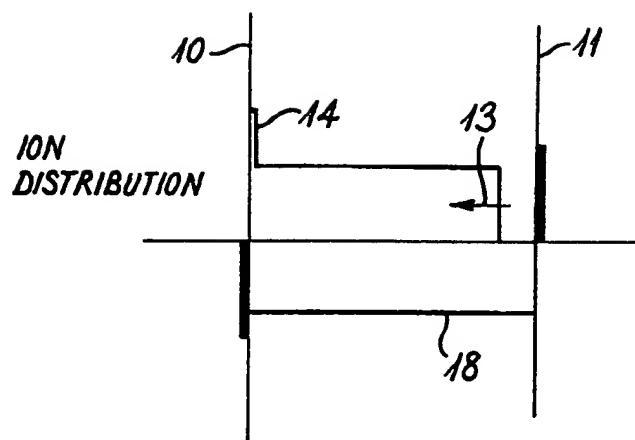


Fig. 1a

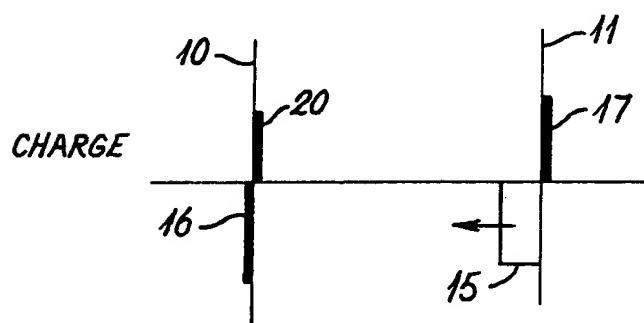


Fig. 1b

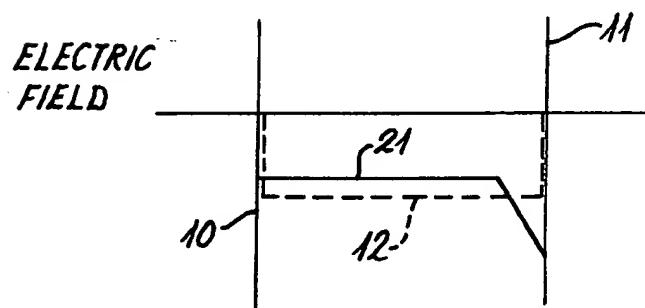


Fig. 1c

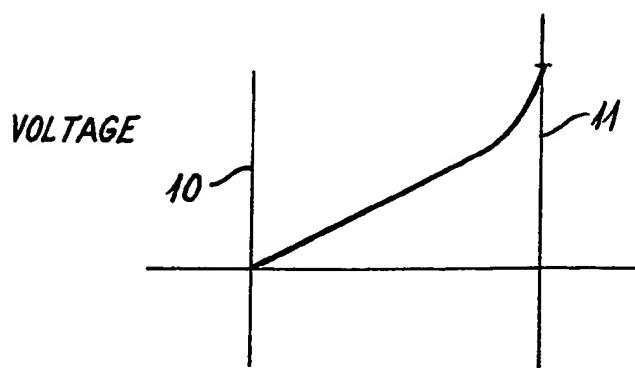


Fig. 1d

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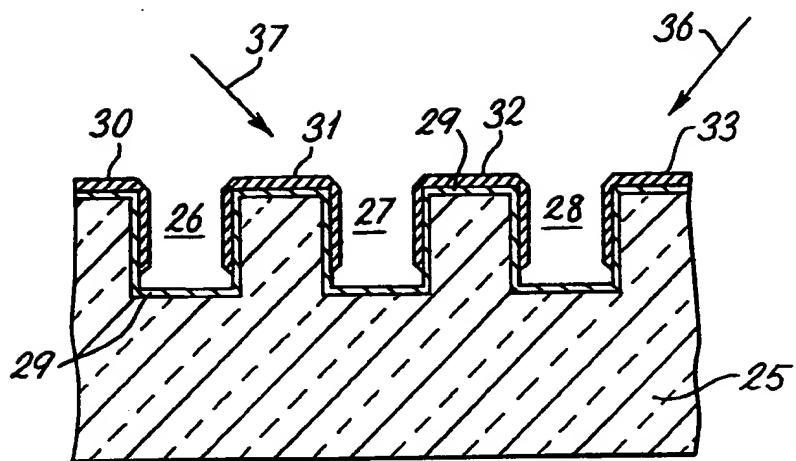


Fig. 2a

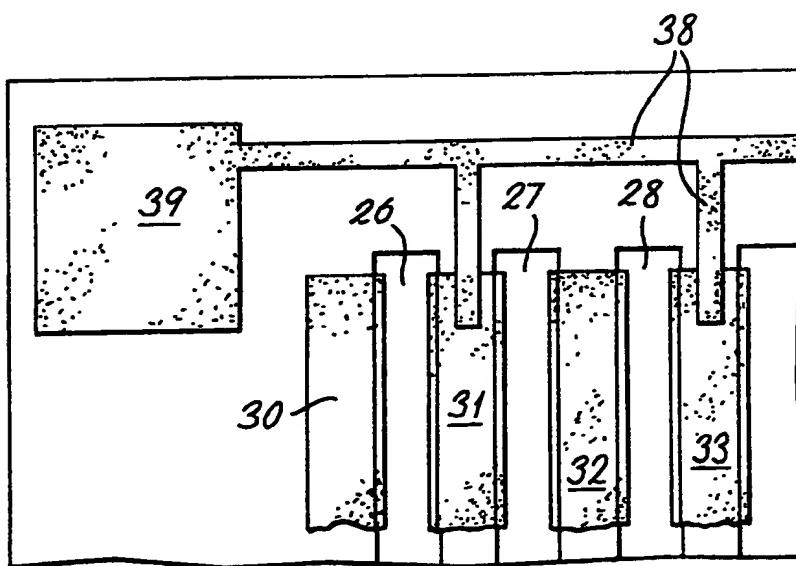


Fig. 2b

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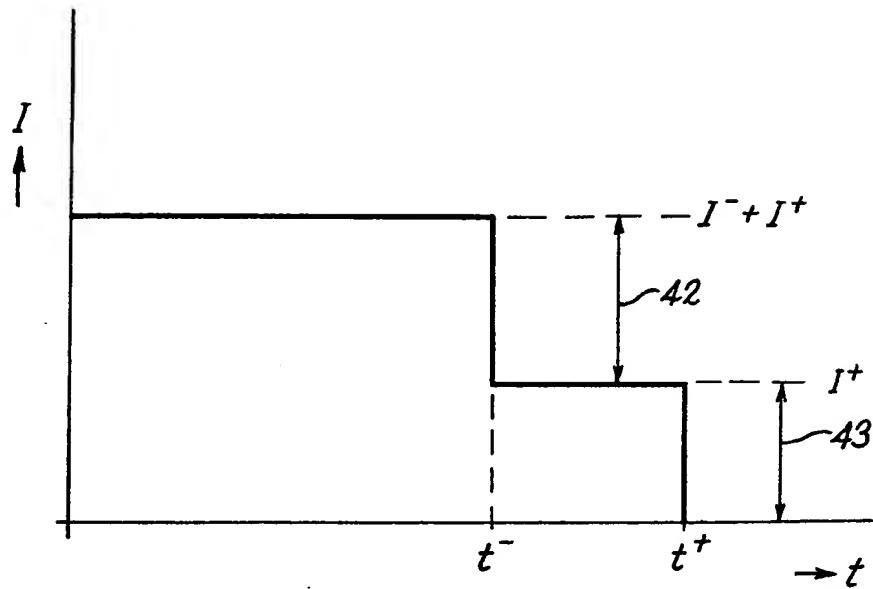


Fig. 3

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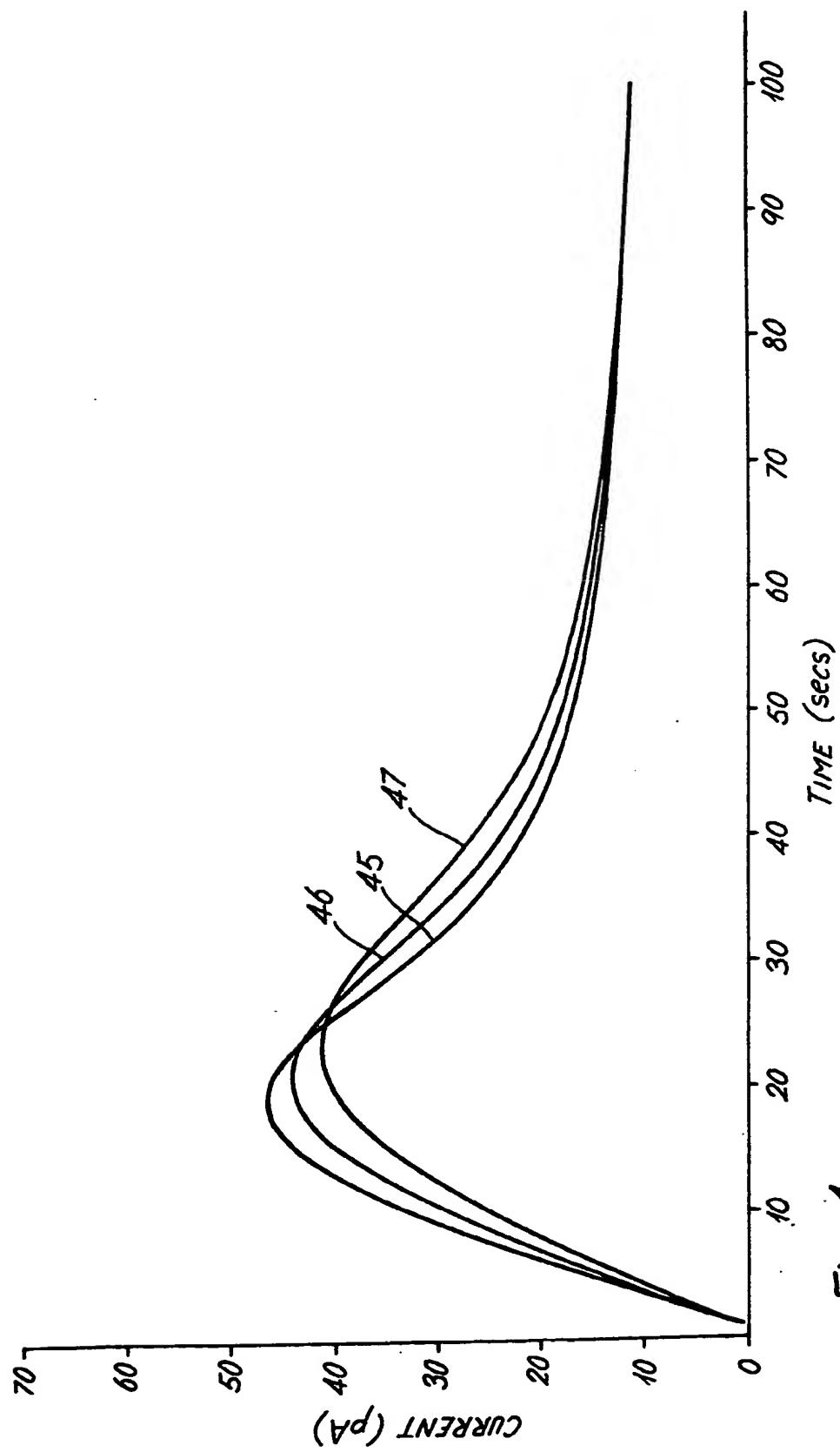


Fig. 4

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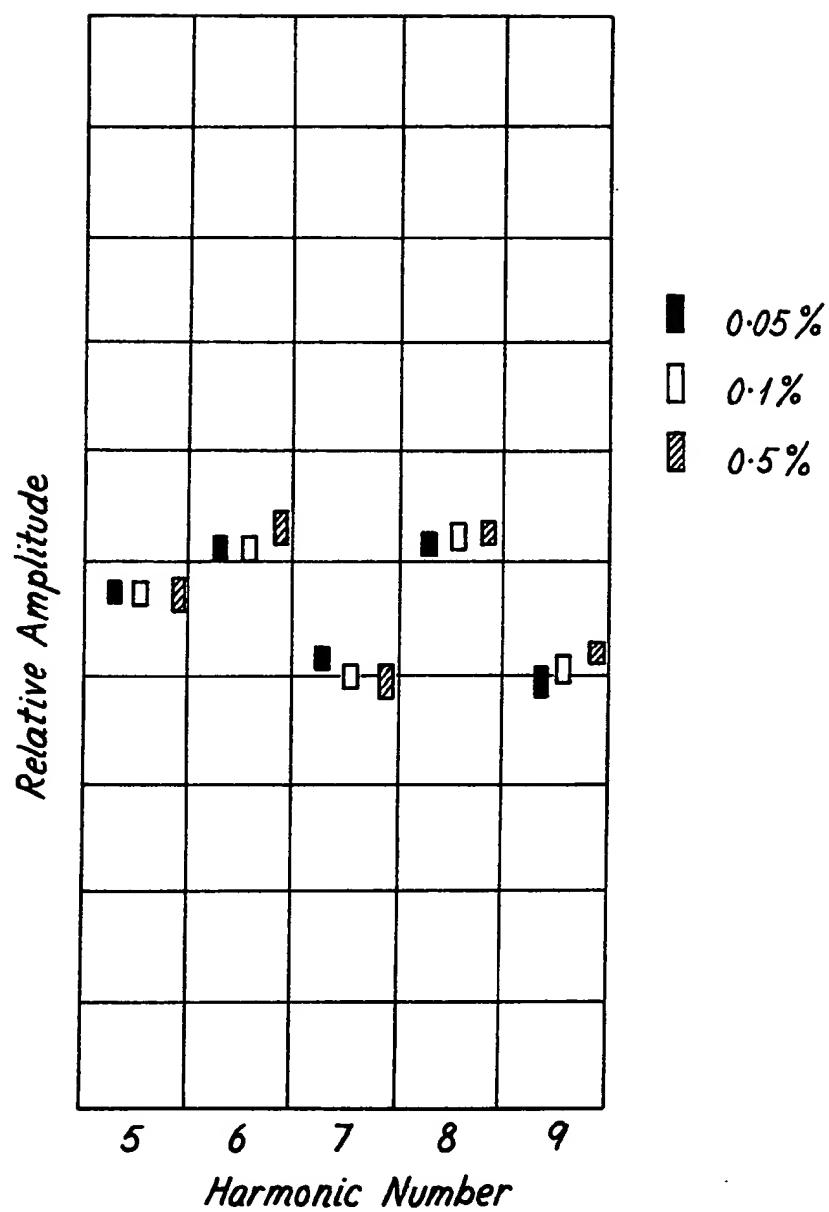


Fig. 5

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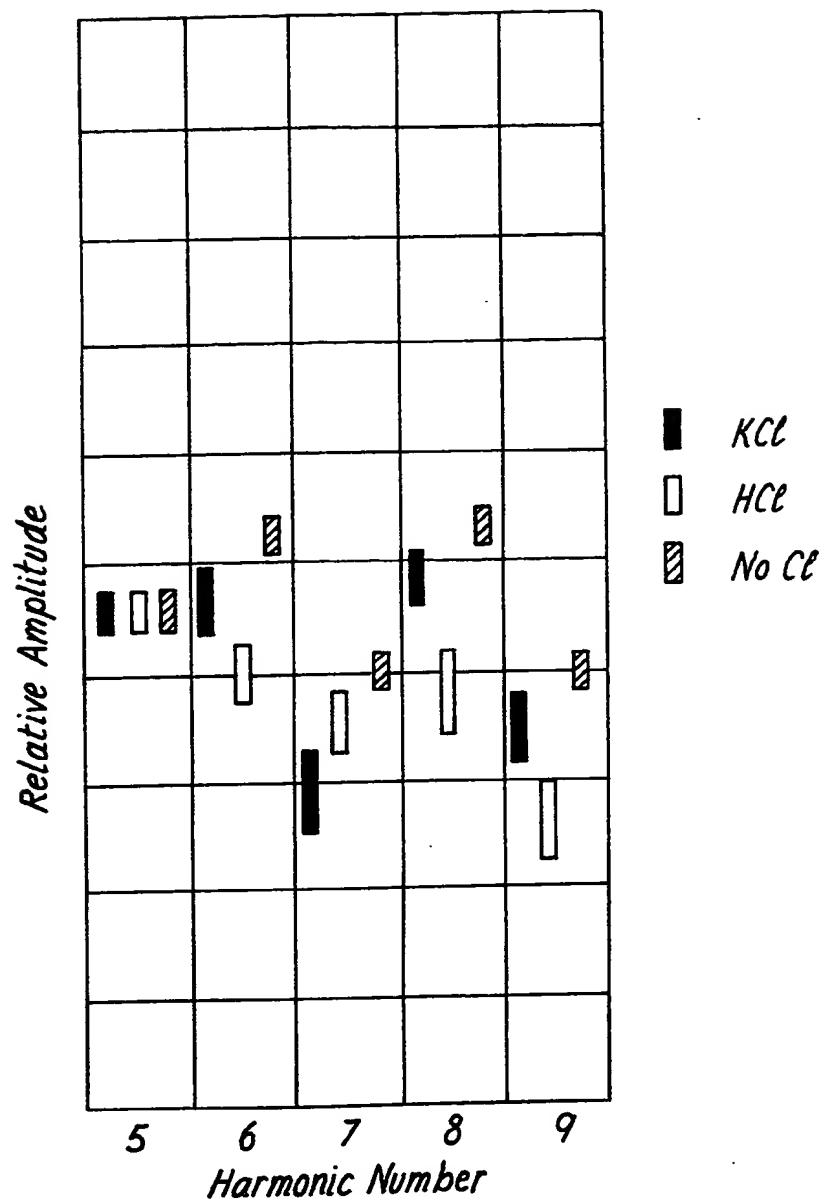


Fig. 6

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METHOD AND APPARATUS FOR MEASURING THE  
TYPE AND CONCENTRATION OF ION SPECIES IN LIQUIDS

The present invention relates to a method of measuring the type and/or concentration of ion species in a liquid. The liquid is usually almost pure water but the method can be applied to other liquids which contain ions. The invention is 05 also related to a cell which can be used in carrying out the above mentioned methods.

The measurement of ionic impurities in water is typically carried out by measuring the d.c. conductance, or the a.c. conductance at a specific frequency. The current flow, and 10 hence the measured conductance is directly related to the density of ionic impurities present.

The measured conductance is, however, related to the aggregate impurity concentration only and does not contain information which enables the discrimination of specific ionic 15 species.

Another method of measuring the level of ionic and molecular impurities in water is described in a paper entitled "Water Inspection Using Capacity and Resistance Measurement" by H. Wöbking, OIZ, Volume 24, 1981, No. 10, pages 361 to 366. As 20 is apparent from the title capacity measurements are used and the object is to determine the ion content of an electrolyte solution. However the types of ion present and their concentrations are not measured.

It is often important to be able to distinguish between 25 these ionic impurities, for example in the evaluation of water purity in the semiconductor industry where it is much more important to eliminate some impurities than others. In studying the effects of acid rain the various acids present in rain water are ionic when in solution and a method is needed for measuring 30 the concentrations of different contaminants so that their effects can be found.

According to a first aspect of the present invention there is provided a method of identifying ion species in a liquid, comprising the steps of

05 placing two spaced-apart electrodes in contact with the liquid,

10 applying a voltage between the electrodes which is greater than  $qNd^2/2\epsilon$ , where  $q$  = the charge on an electron,  $N$  is the highest expected concentration of the ion in the liquid,  $\epsilon$  is the permittivity of the liquid and  $d$  is the distance between the electrodes, and

15 obtaining an indication of the interval between the cessation of a charging current, flowing through the electrodes and charging the capacitance between the electrodes when the said voltage is applied, and a subsequent fall in the substantially constant current which flows through the electrodes after the charging current has ceased.

Provided the above mentioned voltage condition is met when a voltage is applied to a liquid which contains ionic impurities then an initial capacitive charging current first flows and this 20 is followed by a constant current during the transit of the most mobile ion species to one of the electrodes. At the end of this interval which it can be shown equals  $d^2/\mu V$ , where  $\mu$  is the mobility of the most mobile species, a sudden drop in the constant current occurs. Thus by measuring the interval the 25 mobility of the species can be calculated and its type can then be found from known mobilities. Often there will be several ion species in the liquid and so the constant current decreases in a series of steps each corresponding to a different species.

According to a second aspect of the present invention there 30 is provided a method of measuring the concentration of an ion species in a liquid, comprising the steps of

placing two spaced-apart electrodes in contact with the liquid,

applying a voltage between the electrodes which is greater than  $qNd^2/2\epsilon$ , where  $q$  = the charge on an electron,  $N$  is the highest expected concentration of the ion in the liquid,  $\epsilon$  is the permittivity of the liquid and  $d$  is the distance between the electrodes, and

05 obtaining an indication of the magnitude of the current which flows through the electrodes after the cessation of a charging current which charges the capacitance between the electrodes when the said voltage is applied.

10 The current which flows after the charging current is proportional to the concentration of all the ion species present in the liquid. At each step reduction in current the size of the step is proportional to the concentration of the species having a transit time which is completed at that step.

15 Usually it will be convenient to carry out both the first and second aspects of the invention together.

Since it is expected that the types and concentrations of ionic impurities in water are likely to be the most useful application, the liquid usually includes or is substantially 20 composed of water.

The methods have the advantages that the concentrations of individual ion species can be measured and their types identified. In addition simple physical interpretation of results is achieved with the transit times and current levels 25 occurring well within the normal capabilities of measurement techniques. The method does however depend upon achieving a cell design with a small electrode spacing otherwise the voltage  $V$  is so high that it is impossible to achieve or is dangerous.

30 Thus according to a third aspect of the present invention there is provided a cell for use in determining the concentration of ion species and/or the type of ion species in a liquid containing that species, comprising  
means for containing a liquid, and

05 a pair of electrodes spaced apart by a distance  $d$  which satisfies the condition  $V > qNd^2/2\epsilon$  where  $N$  is the maximum concentration for which the cell may be used,  $V$  is a voltage which is of a practical value and can be used substantially safely in making measurements,  $q$  is the charge on an electron and  $\epsilon$  is the permittivity of the liquid.

10 The voltage  $V$  depends on circumstances and normally a safe voltage might be considered as being below, say, 50 or perhaps even 100 volts but if suitable precautions are taken voltage  $V$  could be 1,000 volts or even higher.

According to a third aspect of the present invention there is provided a method of identifying ion species in a liquid, comprising the steps of

15 placing two spaced-apart electrodes in contact with the liquid,

applying a cyclically varying voltage between the electrodes, analysing the harmonic content of the current which flows between the electrodes, and

20 comparing the pattern of harmonics obtained with known patterns for one or more ion species.

According to a fourth aspect of the present invention there is provided a method for use in determining the type and/or concentration of ion species in a liquid, comprising the steps of

25 placing two spaced-apart electrodes in contact with the liquid,

applying a voltage which varies in time in one sense between the electrodes,

30 obtaining an indication of the variation with time of the current which flows between the electrodes when the said voltage is applied, and

comparing the said current variation with known variations for one or more ion species.

Certain embodiments of the invention will now be described with reference to the accompanying drawings in which:-

Figures 1a to 1d illustrate ion, charge, electric field and voltage distributions, respectively, for water containing a single mobile ion between two electrodes when a step voltage is applied to the electrodes,

05 Figures 2a and 2b show a part cross-section and part plan view of a cell according to the invention,

Figure 3 illustrates currents which flow between two electrodes when all mobile ions in a solution move to the electrodes,

10 Figure 4 shows theoretical transient currents expected to flow between two electrodes in contact with a solution containing a mobile ion when a ramp voltage is applied to the electrodes,

15 Figure 5 shows the relative amplitudes of harmonics in current which flows between two electrodes in contact with solutions of different concentrations of NaCl when a sinusoidal voltage is applied between the electrodes, and

20 Figure 6 shows the relative amplitudes of harmonics in current which flows between two electrodes in contact with solutions of NaCl, KCl and HCl when a sinusoidal voltage is applied between the electrodes.

Figures 1a to 1d show the situation a short time after a step voltage has been applied between negative and positive electrodes represented spatially by the lines 10 and 11, respectively, and separated by a liquid containing a single ionic impurity. The initial electric field when the step voltage is applied is shown by the dashed line 12 in Figure 1c. The electric field causes movement of the most mobile ions which are assumed to be positive towards the negative electrode as shown by the arrow 13 in Figure 1a. Positive ions accumulate on the negative electrode as indicated at 14 leaving a negative space charge 15 near the positive electrode. The lines 16 and 17 represent the charge on the electrodes as a result of the applied voltage and the line 18 is a negative charge which balances the ionic charge, on the assumption that before the step voltage is applied the liquid between the electrodes is electrically neutral.

As the ionic charge 20 corresponding to the ions accumulated at the negative electrode increases, the electric field in that part of the liquid still containing positive ions decreases as shown by the horizontal portion of the line 21 (Figure 1c) so 05 that the rate of increase of the charge 20 decreases as time progresses.

Two possibilities then exist: either the space charge widens to the cell width when all the positive ions are drawn to the negative electrode, or the electric field drops to zero 10 somewhere in the liquid (that is the horizontal part of the line 21 reaches zero) and the positive ions no longer move because the space charge has absorbed all the applied voltage.

The applied voltage may be obtained from the charge distribution by a double spatial integration of this charge:

$$15 \quad V = \frac{(Q_1 - Q_2)d}{\epsilon} + \frac{Q_2^2}{2qN\epsilon} \quad \text{equation (1)}$$

where  $Q_1$  and  $Q_2$  correspond to the charges 16 and 20, respectively. When the space charge just extends across  $d$

$$Q_1 - Q_2 = 0$$

and since  $Q_2 = Nqd$ , the voltage ( $V$ ) necessary for all the 20 positive ions to reach the negative electrode is given by

$$V = q \frac{Nd^2}{2\epsilon}$$

This equation gives the minimum voltage necessary to operate the invention although for good results a greater voltage is required. In order to give the voltage  $V$  a practical value the 25 distance  $d$  should be less than about 100  $\mu\text{m}$  and preferably less than 10  $\mu\text{m}$ .

A cell which has a suitable dimension  $d$  is now described and is based on a silicon substrate 25 shown in Figure 2a.

The silicon substrate 25 has vertically sided grooves such as the grooves 26, 27 and 28 etched in (110) silicon or plasma-etched in the substrate. The upper surface of the substrate is oxidised to form a layer 29 and the ridges between the grooves carry electrodes, such as the electrodes 30 to 33.

05 The distance between the electrodes in the vertically sided grooves is typically 2-20  $\mu\text{m}$  and this corresponds to the distance  $d$  mentioned above. Thus if water containing ionic impurities is introduced into the grooves then the condition 10  $V > qNd^2/2\epsilon$  is satisfied for a voltage of less than 50 volts.

10 The process for producing the silicon substrate 25 with grooved upper surface, electrodes, connections and contact pads employs the following steps:-

1. define the grooves photolithographically and etch.
- 15 2. oxidise the upper surface.
3. mask the groove ends.
4. evaporate electrodes at angles corresponding to arrows 36 and 37 in Figure 2a.
5. open windows for a connection 38 and a contact pad 39 (see 20 Figure 2b) and a corresponding connection and contact pad (not shown) for electrodes between those connected by the contact 38.
6. evaporate and define contact metal.

As a result alternate electrodes are connected in parallel, 25 for example the electrodes 26 and 33 are connected in parallel by the connection 38 and the electrodes 30 and 32 are connected by the connection which is not shown in Figure 2b.

In order to determine the types of ion species and their 30 concentrations in a liquid, the liquid is placed in a cell containing the substrate 25 and connections are made to the contact pad 39 and the corresponding contact pad. A voltage step, typically of about 30 volts, is applied between the contact pads with the voltage held at its new value for a time 35 which exceeds the transit times of all ionic species likely to be present in the liquid. A current indicator device is

connected between the voltage source applying the step and one of the contact pads and when the step is applied the current indicator device initially shows a constantly varying charging current charging the capacity between the alternate sets of electrodes and when charging has finished a constant current flows during the transit time of the various species in the liquid.

As expected from the explanation accompanying Figures 1a to 1d, following the initial capacitive charging current, a constant current flows during the transit of the most mobile species to one of the electrodes provided that the condition  $V = qNd^2/2\epsilon$  is met. With this spacing all the ions of the mobile species are drawn to the negative electrode. At the end of this interval which has a duration given by  $d^2/\mu V$ , a sudden drop in current occurs. The interval is measured and the mobility ( $\mu$ ) of that species is calculated so identifying the most mobile species. The next species follows on so giving a series of steps in current each corresponding to a different species. The magnitude of these current steps is related to the concentration of the ions of that species present. In order to give a clear definition of transit time the current waveform may be differentiated to give a series of "spikes" between which transit times can be measured.

An example showing how the invention is expected to perform in practice is now given.

An aqueous solution containing  $\text{Na}^+$  ions, at a concentration of  $2 \times 10^{15} \text{ cm}^{-3}$ , and  $\text{Cl}^-$  ions, at the same concentration, is considered in a cell having dimensions  $d = 3 \mu\text{m}$  and area ( $A$ )  $1 \text{ cm}^2$ . The mobilities  $\mu_p$  and  $\mu_n$  of  $\text{Na}^+$  and  $\text{Cl}^-$  are  $5 \times 10^{-4} \text{ cm}^2/\text{v.s}$  and  $8 \times 10^{-4} \text{ cm}^2/\text{v.s}$ , respectively.

The above two ion species, with the densities specified, would give an overall resistivity of  $10 \text{ M}\Omega$ .

In the limiting case when the field the ions experience is constant at  $V/d$ , ( $V$  is the applied step-voltage), the inequality to be satisfied is

$$\frac{\epsilon AV}{d} \gg 2qNd$$

05 where  $N = N^+ = N^-$ ,  $\epsilon$  is the permittivity  
 $q$  is the ionic charge,  $= 1.6 \times 10^{-19}$  C  
with  $\epsilon = 80 \times 8.85 \times 10^{-14}$  F/cm.

The condition on  $V$  then is that  $V \gg 8$  volts. Thus  $V$  is chosen as 50 V.

10 After the charging current has ceased, that is the current has become constant, the idealised variation of current with time, shown in Figure 3, is expected. The magnitude of the current at 41 is the sum of the currents  $I^-$  and  $I^+$  due to the  $Cl^-$  and  $Na^+$  ions.

15  $I^- = \frac{qN^- \mu nVA}{d} = 42.7$  mA, and

$$I^+ = \frac{qN^+ \mu pVA}{d} = 26.7$$
 mA.

At time  $t^-$  all the  $Cl^-$  ions have reached the positive electrode, and since  $I^-$  depends on  $N^-$  (the concentration of  $Cl^-$  ions) the size of a step 42 indicates the concentration of 20 the  $Cl^-$  ions. The time  $t^-$  is given by

$$t^- = \frac{d^2}{(\mu^-)V} = 2.25 \mu s$$

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Similarly, at time  $t^+$  all the  $\text{Na}^+$  ions have reached the negative electrode and the height of a step 43, given by

15       $I^+ = \frac{qN^+\mu pVA}{d} = 26.7 \text{ mA},$

05      allows the concentration ( $N^+$ ) to be calculated. The time  $t^+$  occurs at

$$t^+ = \frac{d^2}{\mu^+V} = 3.6 \mu\text{s}$$

10      The rectangular form of the current shown in Figure 3 is a limiting case where the condition for  $V$  is well satisfied. If that condition is relaxed the current progressively decreases over  $0 < t < t^-$ , but there is still a sudden drop in current at  $t^-$  which can be detected. Thus it is possible to use higher values of  $d$  and/or lower values of  $V$  and still obtain information about the species type.

15      The rise time for  $V$  should be about one hundredth of the shortest of the times taken for all ions of one type to reach an electrode.

20      The equations for  $I^+$  and  $I^-$  given above are a special case  
 $(\text{that is } V \gg q \frac{Nd^2}{2\epsilon})$  of two equations, which are now derived,  
for the electrode current which flows at time  $t$ .

For a step voltage  $V$  when one ion only moves, the rate of build-up of ions on the negative electrode is given by

$$\frac{dQ_2}{dt} = qNv \quad \text{equation (2)}$$

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where  $v$  is the velocity of ions. If it is assumed that their velocity is related to the electric field by a constant mobility  $\mu$ , then (2) becomes

$$\frac{dQ_2}{dt} = \frac{qN\mu}{\epsilon} (Q_1 - Q_2) \quad \text{equation (3)}$$

- 05 where the electric field, from Gauss' Law, is  $(Q_1 - Q_2)/\epsilon$ .  
Equation (1) may be arranged to give

$$Q_0 = Q_1 - Q_2 + \frac{Q_2^2}{2Q_d} \quad \text{equation (4)}$$

where  $Q_0 = \frac{\epsilon V}{d}$ ,  $Q_d = qN\epsilon$  (Total ionic charge).

- Note that  $Q_0$  and  $Q_d$  are constants.  
10 Substituting for  $Q_1 - Q_2$  from (4) into (3)

$$\frac{dQ_2}{dt} = \frac{qN\mu}{\epsilon} \left( Q_0 - \frac{Q_2^2}{2Q_d} \right) \quad \text{equation (5)}$$

Equation (5) may be solved for  $Q_2$  to give

$$Q_2 = \sqrt{(2Q_dQ_0)} \left[ \frac{e^{\gamma t} - 1}{e^{\gamma t} + 1} \right] \quad \text{equation (6)}$$

where  $\gamma = (\mu/d) (2qVN\epsilon)^{1/2}$

- 15 The resulting electrode current  $I = dQ_1/dt$ , may be obtained by differentiating (4) and substituting for  $Q_2$  and its derivatives using (6):-

$$I = \frac{I_0 e^{\gamma t}}{(1 + e^{\gamma t})^3} \{ 1 + \beta + e^{\gamma t} (1 - \beta) \} \quad \text{equation (7)}$$

where

20  $I_0 = \gamma(8Q_0Q_d)^{1/2}$ ,  $\beta = (2Q_0 Q_d)^{1/2}$

05 This current transient is characterised by  $\gamma$  which is dependent upon the mobility of the moving ion, and therefore differs between species having different mobility. If during sufficient time had elapsed for it to disappear, a second transient would commence, slower than the first, which would be associated with the second most mobile ion. This process would continue until all significant ion species were identified.

10 Unfortunately the assumption that no other ions move during the transient of the most mobile one is not a good one for this simple form of excitation. As the dipole develops the field experienced by the less mobile ions increases as the dipole layer forms so that their velocity is also increased and can exceed that of the more mobile ion.

15 A more general formulation involving two moving ion species and for any voltage excitation is now given. Assuming that the concentrations of both positive and negative ions are constant across the dipole layers, the voltage across the cell is given by solving the Poisson equation.

20 
$$V = \frac{(Q_1 - Q_2 - Q_3)d}{\epsilon} + \frac{Q_2^2}{2qN_B\epsilon} + \frac{Q_3^2}{2qN_A\epsilon} \quad \text{equation (8)}$$

where

$Q_2 = qN_B X_B$ ,  $Q_3 = qN_A X_A$ , and  $X_A$  and  $X_B$  are the widths of the regions free of the ions A and B.

25 If the velocity of the ion is linearly related to the electric field through constant mobilities,  $\mu$  and  $\mu_p$ , then

$$\frac{dQ_2}{dt} = qN_A v = \frac{qN_A \mu_p (Q_1 - Q_2 - Q_3)}{\epsilon} \quad \text{equation (9)}$$

where the electric field experienced by the ion is  $(Q_1 - Q_2 - Q_3)/\epsilon$ .

Similarly,

$$\frac{dQ_3}{dt} = \frac{qN_B\mu_n(Q_1 - Q_2 - Q_3)}{\epsilon} \quad \text{equation (10)}$$

Equations (8), (9) and (10) contain three unknown,  $Q_1$ ,  $Q_2$  and  $Q_3$ .

05 If the applied voltage is held at zero up to some starting value,  $t = 0$ , then the initial values of these unknowns are all zero. If at  $t \geq 0$  some time-dependent waveform is applied, the time evolution of  $Q_1$ ,  $Q_2$ ,  $Q_3$  may be calculated using a finite difference formulation of equations (8), (9) and (10).

10 The theoretical time-dependent current which flows when a linear ramp voltage is applied to a cell containing water having two ions both at the same concentration ( $10^5 \text{ cm}^{-3}$ ) is shown in Figure 4 for three different mobilities:

15 curve 45,  $\mu = 11.2 \times 10^{-4}$ ; curve 46,  $\mu = 9.6 \times 10^{-4}$ ; and curve 47,  $\mu = 8 \times 10^{-4} \text{ cm}^2/\text{v.s.}$  The current peak occurs at a time which depends on mobility and may therefore serve as an indicator of species. The time at which the current peak occurs also varies with concentration and may be used to indicate concentration of a known ion. Fourier transformation of the theoretical transient current shows that the relative magnitudes 20 of harmonics varies with mobility and a particular pattern of transform may be associated with a particular species and so be used to identify it.

25 In a related method of identifying ion species, a sinusoidal voltage is applied to a cell containing water in which the ion species are dissolved. The cell may simply consist of two disc-shaped electrodes of about 8 cms diameter spaced apart by a PTFE annulus about 0.5 cms thick. The current flowing in the cell passes to a dynamic analyser which indicates the relative amplitudes of the harmonics in this current. Figure 5 indicates 30 the harmonic content of NaCl and shows a nearly constant pattern for three concentrations. The different patterns which occur with different ion pairs are illustrated in Figure 6 and

indicate that the species of ion present can be identified if the various patterns can be recognised and if, where several pairs of ions are present, one pattern does not significantly mask another. For Figures 5 and 6, fundamental frequencies and 05 harmonics were in the range 10 Hz to 100 kHz but this range could, in principle, be extended to cover frequencies from 1 Hz to 1 MHz.

Although the invention has been described with one particular cell construction and with the measurement of the 10 impurities in water particularly in mind, it will be realised that other cells can be used provided the above mentioned condition for voltage is met and that other liquids can be used provided they contain ions from, for example, disassociation when a substance is dissolved in the liquid, or a chemical 15 reaction which takes place forming ions when a substance is in contact with the liquid.

CLAIMS

1. A method of identifying ion species in a liquid comprising the steps of

placing two spaced-apart electrodes in contact with the liquid,
- 05 applying a voltage between the electrodes which is greater than  $qNd^2/2\epsilon$ , where q = the charge on an electron, N is the highest expected concentration of the ion in the liquid,  $\epsilon$  is the permittivity of the liquid and d is the distance between the electrodes, and
- 10 obtaining an indication of the interval between the cessation of a charging current, flowing through the electrodes and charging the capacitance between the electrodes when the said voltage is applied, and a subsequent fall in the substantially constant current which flows through the electrodes after the charging current has ceased.
- 15 2. A method according to Claim 1 including obtaining an indication of the magnitude of the current which flows through the electrodes after the cessation of a charging current which charges the capacitance between the electrodes when the said voltage is applied.
- 20 3. A method of measuring the concentration of an ion species in a liquid which contains ions, comprising the steps of

placing two spaced-apart electrodes in contact with the liquid,
- 25 applying a voltage between the electrodes which is greater than  $qNd^2/2\epsilon$ , where q = the charge on an electron, N is the highest expected concentration of the ion in the liquid,  $\epsilon$  is the permittivity of the liquid and d is the distance between the electrodes, and
- 30 obtaining an indication of the magnitude of the current which flows through the electrodes after the cessation of a charging current which charges the capacitance between the electrodes when the said voltage is applied.

4. A cell for use in determining the concentration of ion species and/or the type of ion species in a liquid comprising means for containing a liquid, and  
05 a pair of electrodes spaced apart by a distance d which satisfies the condition  $V > qNd^2/2\epsilon$  where N is the maximum concentration for which the cell may be used, V is a voltage which is of a practical value and can be used substantially safely in making measurements, q is the charge on an electron and  $\epsilon$  is the permittivity of the liquid.
- 10 5. A cell according to Claim 4 wherein the voltage V is not greater than 500 volts.
6. A cell according to Claim 4 wherein the distance d is not greater than 100  $\mu\text{m}$ .
- 15 7. A cell according to Claim 4, 5 or 6 comprising a semiconductor substrate etched to provide at least one groove into which the liquid can enter and carrying electrodes on opposite sides of the groove which are insulated from the substrate.
- 20 8. A cell as hereinbefore described with reference to Figures 1a and 1b of the accompanying drawings.

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